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Extraction With Supercritical Fluid

See **II / EXTRACTION / Supercritical Fluid Extraction**

Inorganic Extractions

See **II / EXTRACTION / Analytical Inorganic Extractions**

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Microwave-Assisted Extraction

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Introduction

Common extraction techniques for solid matrices include Soxhlet extraction, sonication extraction, supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), and accelerated-solvent extraction (ASE).

Soxhlet extraction allows use of large amount of sample (e.g. 10–30 g), no filtration is required after the extraction, the technique is not matrix dependent, and many Soxhlet extractors can be set up to perform in unattended operation. The most significant drawbacks of Soxhlet extraction are: long extraction times (e.g. up to 24–48 h), large amount of solvent usage (300–500 mL per sample), and the need for evaporation after sample extraction.

Sonication extraction is faster than Soxhlet extraction (30–60 min per sample) and allows extraction of large amount of sample with a relatively low cost, but it still uses about as much solvent as Soxhlet extraction, is labour intensive, and filtration is required after extraction.

The newer extraction techniques such as SFE, MAE, and ASE are very attractive because they are a lot faster, use much smaller amounts of solvents, and are environmentally friendly techniques. For example, SFE uses carbon dioxide or modified carbon dioxide (e.g., carbon dioxide containing a small amount of an organic solvent known as modifier) for extraction. Carbon dioxide is a nontoxic, nonflammable, and environmentally friendly solvent. Furthermore, the extraction selectivity can be controlled by varying the pressure and temperature of the supercritical fluid and by the addition of modifiers.

MAE uses microwaves that can easily penetrate into the sample pores causing the solvent trapped in the pores to heat evenly and rapidly. In contrast to conventional heating where it takes a long time for the vessel to heat and then transfer its energy to the

solvent, MAE is very fast since the heat is transferred directly to the solvent (provided that the solvent absorbs microwaves). MAE is promising because: it is fast (e.g. 20–30 min per batch of as many as 12 samples); MAE uses small amounts of solvents as compared to Soxhlet and sonication extraction (30 mL in MAE versus 300–500 mL in Soxhlet extraction); it allows full control of extraction parameters (time, power, temperature); stirring of the sample is possible in MAE; allows high temperature extraction; and no drying agents are needed in MAE since water absorbs microwaves very fast and thus can be used to heat up the matrix. MAE has several drawbacks that contributed to its slow acceptance such as: extracts must be filtered after extraction, which slows down the operation; polar solvents are needed; cleanup of extracts is needed because MAE is very efficient (e.g. 'everything' gets extracted); and the equipment is moderately expensive.

Accelerated solvent extraction is a fairly new extraction method that was approved recently by the U.S. Environmental Protection Agency (EPA) as Method 3545. The extraction is done in a closed-vessel at elevated temperatures (50° to 200°C) and pressures (1500–2000 psi). This technique is attractive because it is fast (e.g. extraction time is approximately 15 min per sample), uses minimal solvent (15–40 mL), no filtration is required after the extraction, and the instrumentation allows extraction in unattended operation. At least 24 samples can be processed sequentially and different sample sizes can be accommodated (e.g. 11, 22, and 33-mL vessels are available).

Theoretical Considerations in MAE

Microwaves are high-frequency electromagnetic waves placed between radio frequency and the infrared regions of the electromagnetic spectrum (their frequency range from 0.3 to 300 GHz corresponding to wavelengths of 1 m to 1 mm). In contrast to conventional heating where the heat penetrates slowly from the outside to the inside of an object, in MAE the heating appears right in the core of the body that is being heated, and the heat spreads from the inside to the outside of that body. The microwave energy affects molecules by ionic conduction and dipole rotation. In ionic conduction, the ions in solution will migrate when an electromagnetic field is applied. The resistance of solution to this flow of ions will result in friction and, thus, heating of the solution. Dipole rotation means realignment of the dipoles with the applied field. At 2450 MHz, the dipoles align and randomize 4.9×10^9 times per second; this forced molecular movement results in molecular 'friction' and, thus, heating of the solution.

Selection of proper solvents is the key to a successful extraction. In selecting solvents, consideration should be given to the microwave-absorbing properties of the solvent, the interaction of the solvent with the matrix, and the analyte solubility in the solvent (the principle of 'like dissolves like' is still applicable in MAE). The larger the dipole moment of the solvent the faster the solvent will heat under microwave irradiation. For example, hexane (dipole moment is < 0.1 Debye) will not heat, whereas acetone with a dipole moment of 2.69 Debye will heat in a matter of seconds. Thus, a mixture of hexane and acetone is an ideal solvent for compounds of environmental significance, and many applications described here use hexane–acetone (1 : 1).

Other important factors under considerations include: 1. the compatibility between the extraction solvent and the analytical method used in the analysis of the extract (the less polar solvents seem to be preferred for gas chromatographic analysis, whereas the more polar ones for liquid chromatographic analysis and immunoassay techniques) and 2. the selectivity of the solvent. Little has been reported in the literature on the selectivity of MAE because the technique is so efficient that it can not be regarded as a selective extraction technique. 'Everything gets extracted' so a cleanup step after the extraction is needed in almost all cases.

When MAE is conducted in closed vessels, the temperature achieved during the extraction will be greater than the boiling points of the solvents. For most of the solvents (e.g. acetone, acetone–hexane, dichloromethane–acetone), the temperature inside the vessel is two to three times the boiling point of the solvent. These elevated temperatures result in improved extraction efficiencies of the analyte from the sample matrix. The reader should refer to **Table 1** for a listing of solvents and their maximum closed-vessel temperatures achieved at 175 psi.

Instrumentation for MAE

The features of commercially available MAE systems are identified in **Table 2**. The equipment (**Figure 1**) used for closed-vessel MAE consists of a magnetron tube, an oven where the individual extraction vessels (closed vessels) are set up on a turntable or rotor, monitoring devices for temperature and pressure, and electronic components. It usually includes specific safety features such as rupture membranes for the extraction vessels, an exhaust fan to evacuate air from the instrument cavity, a solvent vapour detector (monitors the presence of solvent vapour in the

Table 1 Solvent boiling point and closed vessel temperature[a]

Solvent	*Boiling point (°C)*	*Closed vessel temperature (°C) at 175 psi*
Dichloromethane	39.8	140
Acetone	56.2	164
Methanol	64.7	151
Ethanol	78.3	164
Acetonitrile	81.6	194
2-Propanol	82.4	145
Acetone–hexane (1 : 1)	52 +	156
Acetone–cyclohexane (70 : 30)	52 +	160
Acetone–petroleum ether (1 : 1)	39 +	147
Dichloromethane–acetone (1 : 1)	[b]	160[c]
Toluene–methanol (10 : 1)	[b]	110–112[c]
Toluene–methanol (1 : 10)	[b]	146[c]

[a]Adapted from Kingston and Haswell.
[b]Information not available.
[c]Taken from Reference 2.

microwave cavity and shuts off the microwave energy whenever solvent vapour is detected in the instrument cavity), an expansion container (the extraction vessels are connected to this expansion container through vent tubing; in case the membrane ruptures, due to increased pressure in the vessel, then vapour is removed through the rupture vent tube), and an isolator located in the wave guide that diverts reflected microwave energy into a dummy load to reduce the microwave energy within the cavity. One manufacturer of microwave equipment uses resealable vessels. In this case, vessels are placed on a sample rotor and secured with a calibrated torque wrench for uniform pressure. If the pressure exceeds the vessel limits, a spring device (Milestone's patented technology) allows the vessel to open and close quickly, thus releasing the excess pressure. These sample rotors are available with (perfluoroalkoxy)polymer (PFA™) and (tetrafluoroalkoxy)polymer (TFM™) liners with pressure ratings of 435 psi to 1450 psi. Another safety feature which was added to the microwave system is the 'movable wall'. To prevent the door from being blown away, a door frame on spring-loaded, high-impact steel bars was added such that the door moves out and in to release pressure from the microwave cavity.

Typical pressures reached with most closed-vessel systems (first-generation) were 105 psi, but today's technology can handle pressures as high as 1500–1600 psi. A special rotor, which houses six thick-walled vessels capable of working at 1600 psi, is available commercially on several systems, including the CEM's MARS-5, Milestone's Ethos-1600,

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Table 2 Features of commercially available MAE systems[a]

Model/ manufacturer	*Power (watts)*	*Sensors*	*Max. pressure (bar)*	*Vessel volume (mL)*	*Vessel material*	*Number of vessels*	*Max. temp. (°C)*
Multiwave/ Anton Paar GmbH, Austria	1000	Pressure control in all vessels	70	100	TFM/ceramics	12	230
			70	100	TFM/ceramics	6	260
			130	50	TFM/ceramics	6	260
		Infrared temperatue measurement in all vessels	130	50	Quartz	6	300
			130	20	Quartz	6	300
MARS-6/CEM, USA	1500	Infrared temperatue measurement in all vessels	36	100	TFM	14	300
			100	100	TFM	12	300
Ethos 900/1600, Milestone, USA	1600	Pressure control in all vessels	30	120	TFM or PFA	10	240
			100	120	TFM	6	280
		Temperature control in all vessels	30	120	TFM or PFA	12	240
			100	120	TFM	10	280
Model 7195/ O.I. Corp. USA	950		13	90	TFM	12	200
			40	90	TFM	12	200
Soxwave 100/ 3.6 Prolabo, France	250	Temperature control	Open vessel	250	Quartz	1	
			Open vessel	100 or 250	Quartz	6	

[a]Lopez-Avila V (1999) *Critical Reviews in Analytical Chemistry* 29: 195, reprinted with permission of CRC Press, Boca Raton, FL.

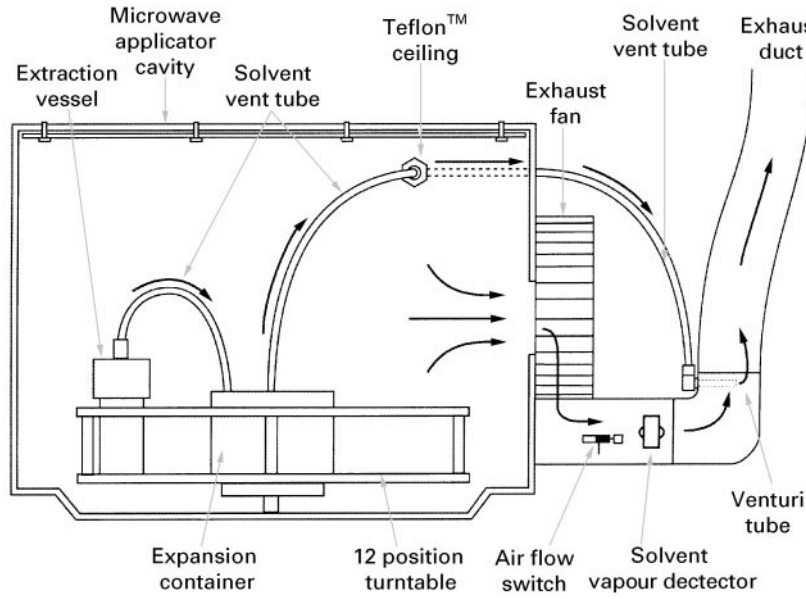

Figure 1 Schematic diagram of a closed vessel MAE system.

and Plazmatronika's UniClever system. In the Milestone system, for example, if the operating pressure inside the vessel exceeds the vessel limits, a special spring device will allow the vessel to open and close, thus reducing the pressure.

The vessels are typically made of microwave transparent materials (e.g. polyetherimide, or TFM) and are lined with perfluoroalkoxy or Teflon™ liners. A new microwave system introduced recently by one manufacturer uses magnetic stir bars, which allow extraction with polar and nonpolar solvents while agitating the sample and solvent to achieve efficient mixing and improve analyte recoveries.

Figure 2 shows a schematic of CEM's lined digestion vessel with and without temperature and pressure control. Vessel body and cap are made of Ultem™, a polyetherimide. The cap and cover of the control vessel are modified to allow

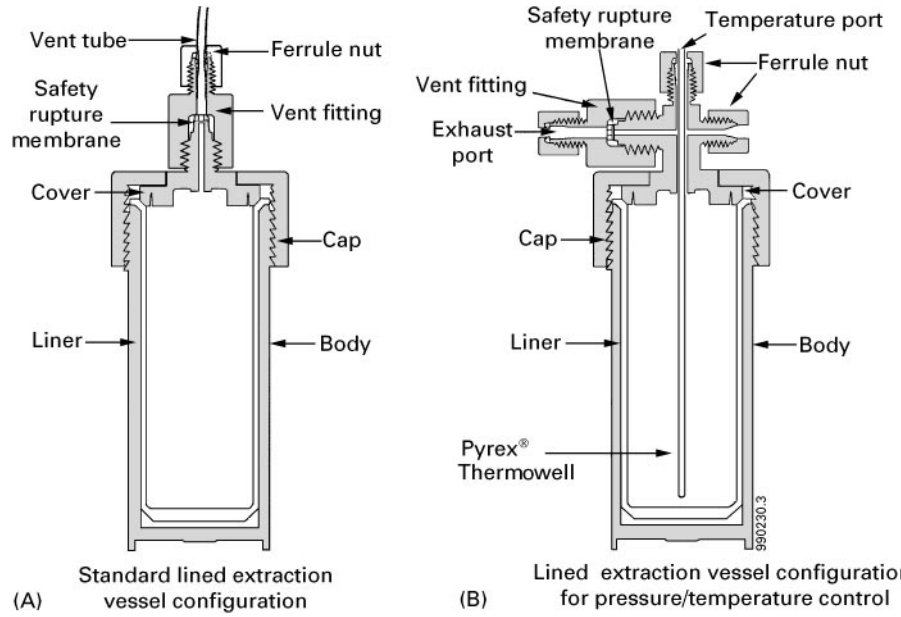

Figure 2 (A) Standard lined extraction vessel and (B) lined extraction vessel with pressure temperature control.

a pressure-sensing tube and a fibre optic temperature probe. The fibre optic probe is microwave transparent and is positioned in the control vessel using a glass thermal well. Infrared temperature sensors are also used to monitor the temperature inside the vessel. As the turntable revolves, the infrared sensor measures the temperature of each vessel. More detail on the pressure and temperature feedback control can be found elsewhere.

Additional features such as magnetic stirring of the extraction solvent inside multiple sample vessels is possible, at least on one commerical system (Ethos 1600 Labstation from Milestone, Inc.), Moreover, nonpolar solvents, such as hexane, can now be heated at elevated temperatures by use of magnetic stir bars made of Milestone's proprietary fluoropolymer Weflon™. (This polymer absorbs the microwave energy and subsequently transfers heat to the surrounding medium.)

All closed vessel systems that are available commercially are multivessel systems which evenly space the vessels on a carousel or rotor and rotate them through a pattern on 360° oscillating turntable.

Specific Applications for MAE

Selected MAE applications are identified in Table 3.

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Polycyclic Aromatic Hydrocarbons (PAHs)

Work done by V. Lopez-Avila *et al.* indicated that PAHs, with the exception of more volatile compounds such as naphthalene, can be extracted quantitatively (recovery > 80%) from soil and sediment matrices with hexane–acetone (1 : 1) at temperatures of 115°C. Typical extraction times for batches of up to 12 samples (5 g each) are 10 min at 100% power (1000 watts). The lower recoveries of naphthalene, acenaphthene, and acenaphthylene were attributed to the presence of water in the soil matrix (to prepare a representative aged soil sample, water was added to the soil matrix to bring its water content to 30%).

Other successful microwave-assisted extractions of PAHs from soils, sediments, and fly ash have been reported with hexane–acetone (1 : 1), acetone alone, dichloromethane alone, dichloromethane–toluene (50 : 50), acetone–petroleum ether (1 : 1), methanol–toluene (9 : 1), and toluene–water.

Dean *et al.* reported on a direct comparison between Soxhlet, MAE, and SFE for PAHs and concluded that the major advantage of MAE is the speed of extraction, but they also acknowledged that without additional cooling after extraction it takes approximately 30 min until the vessels can be opened and extracts processed. Barnabas, Dean and coworkers also investigated the effects of pressure, temperature, extraction time, and percent of methanol modifier added to the extraction solvent in order to optimize the extraction.

Chee *et al.* reported a 5-min heating at 115°C with 30 mL hexane-acetone (1 : 1) as the optimum extraction conditions for a 5 g sample, conditions which are very similar to those reported by V. Lopez-Avila *et al.*

Optimization of MAE of PAHs using open-vessel technology was conducted by Budzinski *et al.*, who reported that the optimum conditions are 30% water, 30 mL dichloromethane, and 10 min heating at 30 W power. When considering that the time needed to reach the boiling point is about 2 min (for dichloromethane), a heating time of 10 min is more than sufficient to extract PAHs quantitatively from the matrix, especially when adding water which is supposed to cause swelling of the matrix.

Organochlorine pesticides (OCPs)

Onuska and Terry extracted aldrin, dieldrin, and DDT from soils and sediments using acetonitrile, isooctane, or a mixture of isooctane–acetonitrile (1 : 1, v/v) and achieved quantitative recoveries using five or seven 30-s irradiations with microwave energy. They also reported that MAE recoveries increases as the moisture content of the soil increases up to 15%. Fish and Revesz used hexane–acetone as extraction solvent and reported that OCP recoveries improved when changing from 1 : 1 hexane–acetone to 2 : 3 hexane–acetone. The latter solvent has a composition similar to the azeotropic vapour in the Soxhlet extractor.

Lopez-Avila *et al.* extracted 45 OCPs from freshly spiked and 24-h aged soil samples with hexane–acetone (1 : 1, v/v). For the freshly spiked soil, 38 compounds had recoveries between 80 and 120%, six compounds had recoveries between 50 and 80%, and the recovery of captafol was above 120%. For the spiked soil samples aged for 24 h, 28 compounds had recoveries between 80 and 120%; 12 compounds had recoveries between 50 and 80%; three compounds including captafol, captan, and dichlone were poorly recovered; and chloroneb and 4,4′-DDT had recoveries above 120%.

When recoveries from freshly spiked soil were compared to those from aged spiked soil, it was found that the recovery of captafol dropped from 122% to 36%, the recovery of captan dropped from 106% to 21%, and the recovery of dichlone dropped from 78% to 10%. Captafol and captan appear to be quite stable upon irradiation of soil/solvent suspensions, but dichlone was found to disappear upon irradiation

Table 3 Selected MAE applications reported in the literature

Analyte	*Matrix*	*Solvent*	*MAE conditions*	*Ref.*
17 PAHs, 14 phenols, 20 organochlorine, 13 miscellaneous compounds (e.g. chlorinated benzenes nitroaromatic compounds and phthalate esters)	3 Reference marine sediments 3 Reference soils Topsoil	Hexane–acetone (1 : 1)	Closed-vessel extraction at 80°C, 115°C for 5, 10, 20 min	2, 3, 4, 41
PAHs	Soil	Acetone–dichloromethane	29 min at 120°C in closed vessel	6
PAHs	Marine sediments Mussel tissue Air particles	Dichloromethane Dichloromethane–toluene (50 : 50) Acetone–hexane (50 : 50)	5 to 40 min irradiation at 30 to 90 W in open vessel, 10 min irradiation at 30 W in open vessel	7
PAHs	Reference marine sediments	Hexane–acetone (1 : 1)	5 min at 115°C in closed vessel	8
PAHs	Reference marine sediments	Dichloromethane	5 to 10 min at 35°C in open vessel	9, 10
PAHs	Fly ash	Hexane–acetone (90 : 10)	70°C in closed vessel	11
PAHs	Soil	Acetone	20 min at 120°C, closed vessel	12
PAHs	Marine sediments	Dichloromethane Acetone–hexane (1 : 1)	5 and 15 min at 115° and 135°C, closed vessel	13
PAHs	Reference marine sediment Reference soil Reference river sediment Reference sewage sludge Industrial soil Marine sediment	Dichloromethane Dichloromethane–toluene (50 : 50) Acetone–hexane (50 : 50, 60 : 40) Acetone	10 min, 30 watts, open vessel	14
Organochlorine pesticides	Sediment saturated with distilled water (1 g sample and 2 mL water)	Acetonitrile Isooctane Isooctane–acetonitrile (1 : 1)	30 s irradiation in open vessel; repeat up to five times	15
16 Phenols, 20 organochlorine pesticides	Topsoil Clay soil Sand Reference soil	Hexane–acetone (1 : 1)	Closed-vessel extraction at 115°C for 10 min	16
16 PAHs 10 Organochlorine pesticides 4 Aroclors 6 Phthalate esters 7 Organophosphorus pesticides 5 Fungicides/herbicides	Water samples preconcentrated on C18 membrane discs	Acetone Dichloromethane	1, 3, 5, 10 min at 80°C, 100°C, 120°C, closed vessel	17
PCB 153	Seal Blubber	*n*-Hexane	Several 30 s extractions at 1000 W	18
PCB 180 PCB 138 *p*,*p*′-DDE Hexachlorocyclohexane Hexachlorobenzene	Pork fat Cold liver	Ethyl acetate–cyclohexane (1 : 1)	Several irradiations at 250 to 1000 W in increments of 100 W	19
PCBs	Municipal sewage sludge	Hexane–acetone (1 : 1)	10 min, 30 W, open vessel	20
PCBs	River sediments	Hexane–acetone (1 : 1)	15 min, closed vessel	21

Table 3 *Continued*

Analyte	*Matrix*	*Solvent*	*MAE conditions*	*Ref.*
C_{16}-C_{32} hydrocarbons 20 PAHs 4 Organochlorine pesticides PCBs	Marine sediments	Toluene–water (1 : 5 to 1 : 2)	6 min, closed vessel	22
Phenol Methyl phenols	Soils	Hexane and hexane–acetone (2 : 8) with pyridine and acetic anhydride for *in-situ* derivatization	130°C in closed vessel	23, 24
Nonyl phenol	Water samples preconcentrated on C18-packed cartridge, C18-packed disc Sediments	Dichloromethane Acetone–petroleum ether (1 : 1)	5 and 15 min at 100°C to 120°C, closed vessel	25
Phenol 2-Chlorphenol 2-Methylphenol 2-Nitrophenol 2,4-Dichlorophenol	Soil	Acetone–hexane (various ratios)	Closed vessel	26
Imidazolinone herbicides	Soil	0.1 M ammonium acetate/ammonium hydroxide (pH 9–10)	3 to 10 min irradiation at 125°C in closed vessel	27–29
Atrazine and degradation products	Lupin seeds Rat feces	Water followed by 0.35 N HCl	Closed vessel, 95–98°C	30
Atrazine Simazine Prometryne	Sandy loam Clay Bentonite Florisil	Methanol Acetone–hexane (1 : 1) Dichloromethane Water		31
Atrazine Simazine Metazachlor Desisopropyl atrazine Desethyl atrazine	Sand Peat Clay	Dichloromethane with water, methanol, and acetonitrite Acetonitrite–0.5% ammonia in water (70 : 30)	5 to 45 min at 30°C to 130°C, 20 min at 115°C	32, 33
Atrazine	Soil	Water	3, 4 and 5 min closed vessel	34
Organotin compounds (mono-, di- and tributyltin; mono-, di- and triphenyltin)	2 Reference sediments	50% acetic acid Isooctane Methanol Water Artificial sea water	1 to 7 min irradiation in open vessel, up to 160 W	35
Organotin compounds	Sediments	0.5 M ethanoic acid in methanol	3 min, open vessel	36
Butyl and phenyl organotin	Reference marine biological matrix Tuna tissue Mussel tissue	25% tetramethyl–ammonium hydroxide in water	3 min at 90°C, 115°C and 130°C, closed vessel	37
Organotin compounds	Sediments	11 M acetic acid $NaBEt_4$	3 min at 50 to 60 W, open vessel	38
Organomercury compounds	Sediments Reference biological materials	2 M nitric acid 2 M hydrochloric acid 25% tetramethyl–ammonium hydroxide	3 min at 60 W, open vessel 2 to 4 min at 40 to 60 W, open vessel	38
Methylmercury	Aquatic sediments Certified reference sediments	Digestion with 6 M HCl (methylmercury is extracted at room temperature by complexation with cysteine acetate and toluene)	10 min at 120°C, closed vessel	39

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of the solvent. (The recovery of dichlone from solvent was only 5.5% after heating at 145°C for 5 min and 2.6% after 20 min at the same temperature.) Microbial degradation may be responsible for the low recoveries of captafol and captan, whereas in the case of dichlone, it is quite likely that this compound is not stable under the conditions used. Nonetheless, these recoveries are higher than those obtained by Soxhlet or sonication extraction.

Water samples can also be extracted by MAE; however, they have to be preconcentrated first on a membrane disc or some adsorbent material. Chee *et al*. used C_{18}-membrane discs and then extracted the discs with 20 mL solvent (acetone and dichloromethane) in a closed-vessel MAE system at 80°C, 100°C and 120°C for 1, 3, 5 and 10 min. Acetone was found to give higher recoveries than dichloromethane. This approach would allow extremely low detection limits since several discs generated by processing a large volume of sample can be extracted in one vessel.

Vetter and coworkers extracted OCPs from fatty tissues (e.g. seal blubber) with solvents such as hexane and ethyl acetate (1 : 1). To transfer heat to hexane, which is microwave transparent, discs of Weflon™ (2.5 cm in diameter × 0.3 cm thickness) were used in the extraction vessel. The yield of extractable fat and recoveries of OCPs after seven irradiation cycles were comparable to those obtained by Soxhlet extraction. Since ethyl acetate–cyclohexane (1 : 1, v/v) seems to extract more fat than hexane, a gel permeation chromatography step after extraction is a must.

Polychlorinated Biphenyls (PCBs)

MAE of PCBs was reported by Lopez-Avila *et al*. Onuska and Terri, Chee *et al*., Pastor *et al*., Dupont *et al*. and Kodba and Marsel. Lopez-Avila *et al*. used hexane–acetone (1 : 1, v/v) and reported that the average recoveries from typical soil matrices were greater than 70% for the Aroclors 1016 and 1260 and the method precision was better than 7%. Furthermore, there was no degradation of PCBs upon heating of solvent/soil suspensions with microwave energy. Three reference materials and 24 soils from a Superfund site, most of which contained Aroclors, were extracted by MAE and analysed by both GC/ECD and enzyme-linked immunosorbent assay (ELISA). Because ELISA is very sensitive and its detection range is quite narrow, the hexane–acetone extracts were first diluted with methanol and subsequently with the assay buffer (which contained 50% methanol) to bring the Aroclor concentrations to less than 5 ng mL^{-1}. These data indicate excellent agreement between the certified Soxhlet/GC/ECD data and the MAE–ELISA data (correlation coefficient 0.9986; slope 1.0168) and the MAE–GC/ECD data and the MAE–ELISA data (correlation coefficient 0.9793; slope 1.0468).

Other solvents used successfully to extract PCBs from environmental samples include isooctane, acetone and dichloromethane, and toluene–water.

Phenols

MAE of phenolic compounds was reported by Lopez-Avila *et al*., Llompart *et al*. Chee *et al*. and Egizabal *et al*. Acetone–hexane seems to be the preferred solvent for 16 phenolic compounds and dichloromethane, acetone–petroleum ether (1 : 1) were reported to work well for extraction of nonylphenol. The only compounds found to degrade during MAE are 2,4-dinitrophenol and 4,6-dinitro-2-methylphenol. MAE recoveries for phenolic compounds are usually higher than the classical extraction method recoveries, and the method precision is significantly better for MAE (e.g. coefficient of variation of 3% for MAE as compared to 15% for Soxhlet and 20% for sonication).

Herbicides

Imidazolinones (e.g. imazapyr, imazmetapyr, imazethapyr, imazaquin, etc.) are extracted from soil with 0.1 M ammonium acetate/ammonium hydroxide (pH 9–10) in a 10-min extraction. A variety of soil samples fortified at 1 to 50 p.p.b. exhibited an average recovery of 92% (standard deviation 13%).

Triazine herbicides have been successfully extracted from soil by MAE with water, methanol, acetone–hexane (1 : 1), dichloromethane, acetonitrile–0.5% ammonia in water (70 : 30), dichloromethane–water (50 : 50), methanol–dichloromethane (10 : 90). Water seems to be preferred since it is very polar solvent and can interact strongly with polar matter in soils to enhance the desorption of triazines; it is a cheap, safe, and environmentally friendly solvent; and it heats up very quickly when irradiated with microwave energy microwave energy. Xiong *et al*. reported that direct heating of soil with water gave a 73.4% recovery for atrazine from soil and, therefore, stated that 'MAE is not only a simple heating'.

Organotin and Organomercury Compounds

Methods reported in the literature for the determination of organotin compounds in soils use extraction with organic solvents in the presence of complexing agent, or leaching with acetic or hydrochloric acid assisted by sonication or some sort of shaking.

Open-vessel MAE was recommended to accelerate the leaching with 50% acetic acid aqueous solution, and the data showed that a 3-min irradiation at 60 W was sufficient to recover tributyl tin from certified reference sediments. Ethanoic acid (0.5 M in methanol) was also reported. When dealing with biological matrices (e.g., tuna tissue, mussel tissue), solubilization with tetramethylammonium hydroxide (TMAH) for a 3 min at 90°C, 115°C, and 130°C in a closed vessel was demonstrated to be as efficient as the hot-plate procedure. Schmitt *et al*. reported on the integration of the solubilization step with the derivatization/extraction step by using 11 M acetic acid for solubilizationm and $NaBEt_4$ for derivatization using an open vessel MAE system.

Organomercury compounds can be extracted from sediments with 6 M hydrochloric acid at 120°C for 10 min in closed vessel or 2 M nitric acid and 2 M hydrochloric acid after 3 min irradiation at 60 W in open vessel. Pure acetic acid and 1 M sulfuric acid could only extract 85% and 55%, respectively. Microwave-assisted digestion of the biological tissue with 25% TMAH for 2–4 min at 40–60 W gave quantitative recovery of both organomercury and inorganic mercury.

Additives in Polymers

Antioxidants such as the Irganox 1010, Irganox 1076, and Irgaphos 168, which are added to polymers to protect them during end-use applications, can be extracted with $>95\%$ efficiency by MAE with *n*-heptane–acetone in a few minutes. Higher temperatures (e.g. 140°C) were used by Jordi *et al*. with cyclohexane–chloroform–triethylamine (45 : 45 : 10) to dissolve polyethylene and extract compounds such as Tinuvin 770, Tinuvin 622, Tinuvin 144, and Chimasorb 81.

Natural Products

Extraction of oils from mint leaves and other materials of biological origin is a patented process known as the 'microwave-assisted process'. Other reports on MAE of natural products include that of Young, Bichi *et al*. and Mattina *et al*. Young extracted ergosterol from fungi and spores by MAE with methanol and 2 M sodium hydoxide. Bichi *et al*. extracted pyrrolizidine alkaloids from Senecio palvadosos and Senecio cordatus dried plants by MAE with methanol at 65 to 100°C for 20 to 30 min. Mattina *et al*. reported on the extraction of taxanes from Taxus biomass by MAE with ethanol. Using 5 g of freshly harvested needles (moisture content 55 to 65%) soaked in 5 mL of water prior to MAE and 10 mL ethanol at 85°C for 9 min resulted in about 90% recovery. This procedure would significantly reduce the costs of the extraction of taxanes from biomass with no reduction in the extraction yields.

See also: **II/Extraction:** Supercritical Fluid Extraction; Ultrasound Extractions. **III/Environmental Applications:** Soxhlet Extraction. **Solid-Phase Extraction with Disks.**

Further Reading

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Multistage Countercurrent Distribution

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Theory

The separation of chemical compounds by partitioning between two liquid phases, so-called liquid–liquid extraction, can be made more effective by using it as a cascade process. One way in which this can be carried out is by multiplicative partitioning, also called countercurrent distribution (CCD). This process, in which complete partition equilibrium is achieved in each step, is presented schematically in **Figure 1**. The principle is that two sets of liquid phases, the upper and lower phase, come into contact with each other stepwise. The bottom phases are numbered 0, 1, 2 and so on. The sample to be analysed (fractionated) is included in the first system (containing bottom phase number 0). Before each transfer of the upper phases (to the right in Figure 1) the two-phase systems are equilibrated by mixing and the sample components are distributed between each pair of phases (each full two-phase system). The partitioning of a pure substance between the phases of a two-phase system can be expressed either by a partition coefficient, K, defined as the ratio of the concentrations (C) of the component in the phases:

$$K = \frac{C\ (\text{in phase I})}{C\ (\text{in phase II})} \qquad [1]$$

or by a partition ratio, G, defined as the ratio of the masses (m) of the components in the phase:

$$G = \frac{m\ (\text{in phase I})}{m\ (\text{in phase II})} \qquad [2]$$

K and G are related by eqn [3]:

$$G = K\frac{\text{Volume (phase I)}}{\text{Volume (phase II)}} \qquad [3]$$

In the following the upper phase is chosen as phase I. A convenient way of analysing the CCD process is to calculate the amounts (in fractions) of a pure